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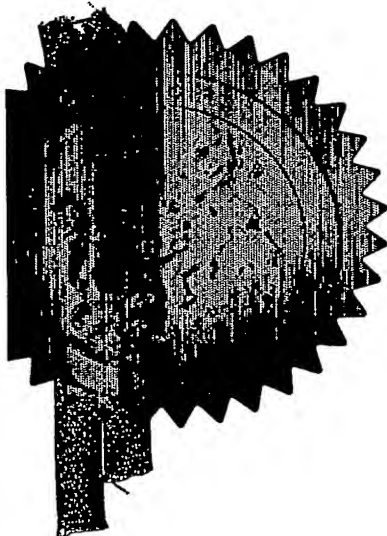
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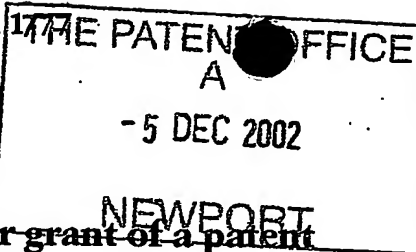


Signed

Stephen Hordley

Dated

14 January 2004



05DEC02 1777 768670-1 C12133
POT/000 0.00-0228335.6

Request for grant of a patent

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Cardiff Road
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1. Your reference

470a

2. Patent application number

(The Patent Office will fill in this part)

0228335.6

05 DEC 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

ELAM-T LIMITED
103 BOROUGH ROAD
LONDON
SE1 0AA

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

810 528 0001

4. Title of the invention

ELECTROLUMINESCENT MATERIALS AND DEVICES

5. Name of your agent (if you have one)

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

COHEN, ALAN NICOL
2 GROVE PLACE
TATSFIELD
Nr. WESTERHAM
KENT

Patents ADP number (if you know it)

TN16 2BB
696 3557001

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)

Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
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See note (d).

Patents Form 1/77

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Description

Claim(s)

Abstract

Drawing(s)

19

4

1

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10. If you are also filing any of the following, state how many against each item.

Priority documents

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Statement of inventorship and right to grant of a patent (*Patents Form 7/77*)

Request for preliminary examination and search (*Patents Form 9/77*)

Request for substantive examination (*Patents Form 10/77*)

Any other documents
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11. I/We request the grant of a patent on the basis of this application.

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A. N. Cohen

01959 577172

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Electroluminescent Materials and Devices

The present invention relates to electroluminescent materials and devices incorporating electroluminescent materials.

5

Materials which emit light when an electric current is passed through them are well known and used in a wide range of display applications. Liquid crystal devices and devices which are based on inorganic semiconductor systems are widely used, however these suffer from the disadvantages of high energy consumption, high cost
10 of manufacture, low quantum efficiency and the inability to make flat panel displays.

Organic polymers have been proposed as useful in electroluminescent devices, but it is not possible to obtain pure colours, they are expensive to make and have a relatively low efficiency.

15

Another compound which has been proposed is aluminium quinolate, but this requires dopants to be used to obtain a range of colours and has a relatively low efficiency.

20

Patent application WO98/58037 describes a range of lanthanide complexes which can be used in electroluminescent devices which have improved properties and give better results. Patent Applications PCT/GB98/01773, PCT/GB99/03619, PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 describe electroluminescent complexes, structures and devices using rare earth
25 chelates.

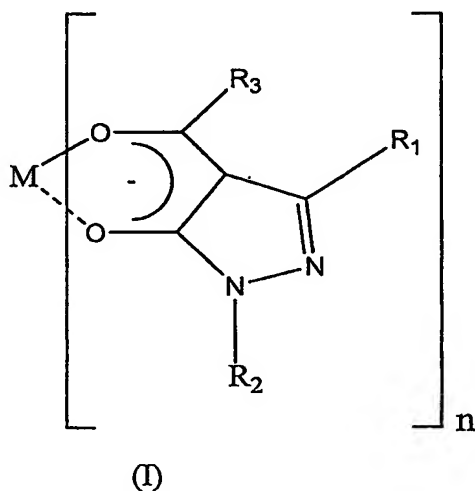
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Hitherto electroluminescent metal complexes have been based on a rare earth, transition metal, lanthanide or an actinide or have been quinolates such as aluminium quinolate.

30

We have now invented electroluminescent materials which do not include a rare earth, transition metal, lanthanide or an actinide.

According to the invention there is provided an electroluminescent compound which
5 has the formula



10 where M is a metal other than aluminium; n is the valency of M; R₁, R₂ and R₃ which may be the same or different are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aliphatic groups substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile; R₁ and R₃ can also
15 be form ring structures and R₁, R₂ and R₃ can be copolymerisable with a monomer e.g. styrene.

The invention also provides an electroluminescent device comprising (i) a first electrode, (ii) an electroluminescent layer comprising a layer of a complex of
20 formula (I) and (iii) a second electrode.

Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.

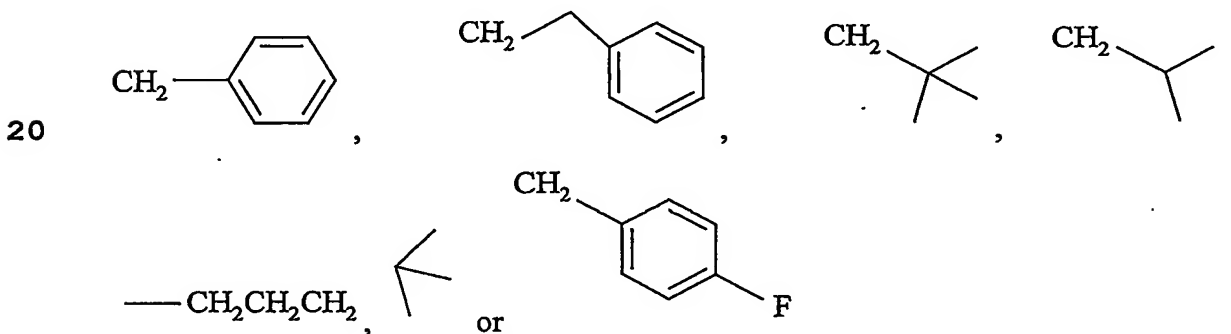
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Preferably R_1 and R_2 are Ph_1 and Ph_2 and at least one of Ph_1 and Ph_2 is a substituted or unsubstituted aromatic compound and the other Ph moiety is selected from hydrogen, and substituted and unsubstituted hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine; substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable with a monomer e.g. styrene. fluorocarbons such as trifluoromethyl groups, halogens such as fluorine. Examples include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole

10

15

Preferably R_1 is methyl and R_2 is



Preferred metals are metals other than aluminium e.g. gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV),

25

platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, yttrium, and R₃ is preferably a phenyl or substituted phenyl group.

- 5 Preferably there is a hole transmitting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transmitting layer. The hole transmitting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

10

Hole transmitting layers are used in small molecule based polymer electroluminescent devices and in electroluminescent devices based on rare earth metal complexes and any of the known hole transmitting materials in film form can be used.

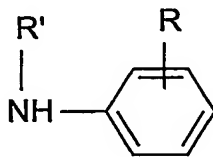
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Hole transmitting layers are used in polymer electroluminescent devices and any of the known hole transmitting materials in film form can be used.

20

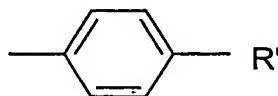
The hole transmitting layer can be made of a film of an aromatic amine complex such as poly (vinylcarbazole), N, N'-diphenyl-N, N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), an unsubstituted or substituted polymer of an amino substituted aromatic compound, a polyaniline, substituted polyanilines, polythiophenes, substituted polythiophenes, polysilanes etc. Examples of polyanilines are polymers of

25



(II)

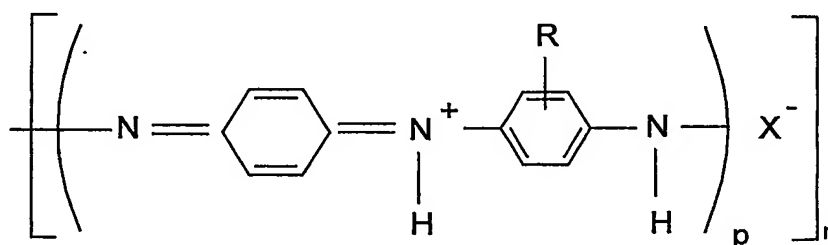
where R is in the ortho - or meta-position and is hydrogen, C1-18 alkyl, C1-6 alkoxy, amino, chloro, bromo, hydroxy or the group



5

where R is alkyl or aryl and R' is hydrogen, C1-6 alkyl or aryl with at least one other monomer of formula I above.

Polyanilines which can be used in the present invention have the general formula



10

(III)

where p is from 1 to 10 and n is from 1 to 20, R is as defined above and X is an anion, preferably selected from Cl, Br, SO₄, BF₄, PF₆, H₂PO₃, H₂PO₄, arylsulphonate, arenedicarboxylate, polystyrenesulphonate, polyacrylate
15 alkylsulphonate, vinylsulphonate, vinylbenzene sulphonate, cellulosesulphonate, camphor sulphonates, cellulose sulphate or a perfluorinated polyanion.

Examples of arylsulphonates are p-toluenesulphonate, benzenesulphonate, 9,10-anthraquinone-sulphonate and anthracenesulphonate, an example of an
20 arenedicarboxylate is phthalate and an example of arenecarboxylate is benzoate.

We have found that protonated polymers of the unsubstituted or substituted polymer of an amino substituted aromatic compound such as a polyaniline are difficult to evaporate or cannot be evaporated, however we have surprisingly found that if the

unsubstituted or substituted polymer of an amino substituted aromatic compound is de-protonated it can be easily evaporated i.e. the polymer is evaporable.

5 Preferably evaporable de-protonated polymers of unsubstituted or substituted polymer of an amino substituted aromatic compound are used. The de-protonated unsubstituted or substituted polymer of an amino substituted aromatic compound can be formed by deprotonating the polymer by treatment with an alkali such as ammonium hydroxide or an alkali metal hydroxide such as sodium hydroxide or potassium hydroxide.

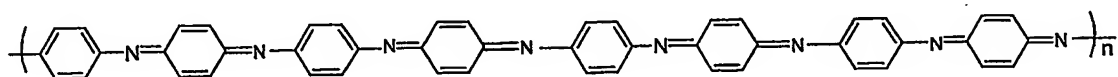
10 The degree of protonation can be controlled by forming a protonated polyaniline and de-protonating. Methods of preparing polyanilines are described in the article by A. G. MacDiarmid and A. F. Epstein, Faraday Discussions, Chem Soc.88 P319 1989.

15 The conductivity of the polyaniline is dependant on the degree of protonation with the maximum conductivity being when the degree of protonation is between 40 and 60% e.g. about 50% for example.

Preferably the polymer is substantially fully de-protonated

20

A polyaniline can be formed of octamer units i.e. p is four e.g.



25

The polyanilines can have conductivities of the order of 1×10^{-1} Siemen cm^{-1} or higher.

30 The aromatic rings can be unsubstituted or substituted e.g. by a C1 to 20 alkyl group such as ethyl.

5 The polyaniline can be a copolymer of aniline and preferred copolymers are the copolymers of aniline with o-anisidine, m-sulphanilic acid or o-aminophenol, or o-toluidine with o-aminophenol, o-ethylaniline, o-phenylene diamine or with amino anthracenes.

10 Other polymers of an amino substituted aromatic compound which can be used include substituted or unsubstituted polyaminonaphthalenes, polyaminoanthracenes, polyaminophenanthrenes, etc. and polymers of any other condensed polyaromatic compound. Polyaminoanthracenes and methods of making them are disclosed in US Patent 6,153,726. The aromatic rings can be unsubstituted or substituted e.g. by a group R as defined above.

15 The polyanilines can be deposited on the first electrode by conventional methods e.g. by vacuum evaporation, spin coating, chemical deposition, direct electrodeposition etc. preferably the thickness of the polyaniline layer is such that the layer is conductive and transparent and can be preferably from 20nm to 200nm. The polyanilines can be doped or undoped, when they are doped they can be dissolved in a solvent and deposited as a film, when they are undoped they are solids and can be
20 deposited by vacuum evaporation i.e. by sublimation.

The structural formulae of some other hole transmitting materials are shown in Figures 1, 2, 3, 4 and 5 of the drawings, where R, R₁, R₂ and R₃ can be the same or different and are selected from hydrogen, and substituted and unsubstituted
25 hydrocarbyl groups such as substituted and unsubstituted aliphatic groups, substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups; R₁, R₂ and R₃ can also form substituted and unsubstituted fused aromatic, heterocyclic and polycyclic ring structures and can be copolymerisable
30 with a monomer e.g. styrene. X is Se, S or O, Y can be hydrogen, substituted or

unsubstituted hydrocarbyl groups, such as substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorine, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile.

- 5 Examples of R_1 and/or R_2 and/or R_3 include aliphatic, aromatic and heterocyclic alkoxy, aryloxy and carboxy groups, substituted and substituted phenyl, fluorophenyl, biphenyl, phenanthrene, anthracene, naphthyl and fluorene groups alkyl groups such as t-butyl, heterocyclic groups such as carbazole.
- 10 The hole transporting material can optionally be mixed with the electroluminescent material in a ratio of 5 - 95% of the electroluminescent material to 95 to 5% of the hole transporting compound.

Other hole transporting materials which can be used are conjugated polymers.

15

US Patent 5807627 discloses an electroluminescence device in which there are conjugated polymers in the electroluminescent layer. The conjugated polymers referred to are defined as polymers for which the main chain is either fully conjugated possessing extended pi molecular orbitals along the length of the chain or

20 else is substantially conjugated, but with interruptions to conjugation, either random or regular along the main chain. They can be homopolymers or copolymers.

The conjugated polymer used can be any of the conjugated polymers disclosed or referred to in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

25

The conjugated polymers disclosed are poly (p-phenylenevinylene)-PPV and copolymers including PPV. Other preferred polymers are poly(2,5 dialkoxyphenylene vinylene) such as poly (2-methoxy-5-(2-methoxypentyloxy)-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy)-1,4-phenylenevinylene) and other poly(2,5

30

dialkoxyphenylenevinylenes) with at least one of the alkoxy groups being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes, polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes, ploythiophenes and oligothiophenes.

5

In PPV the phenylene ring may optionally carry one or more substituents e.g. each independently selected from alkyl, preferably methyl, alkoxy, preferably methoxy or ethoxy.

10 Any poly(arylenevinylene) including substituted derivatives thereof can be used and the phenylene ring in poly(p-phenylenevinylene) may be replaced by a fused ring system such as anthracene or naphthlyene ring and the number of vinylene groups in each polyphenylenevinylene moiety can be increased e.g. up to 7 or higher.

15 The conjugated polymers can be made by the methods disclosed in US 5807627, PCT/WO90/13148 and PCT/WO92/03490.

The hole transmitting material and the light emitting metal compound can be mixed to form one layer e.g. in an proportion of 5 to 95% of the hole transmitting material to 95 to 5% of the light emitting metal compound.

20

Optionally there is a layer of an electron transmitting material between the cathode and the electroluminescent material layer, the electron transmitting material is a material which will transport electrons when an electric current is passed through electron transmitting materials include a metal complex such as a metal quinolate e.g. an aluminium quinolate, lithium quinolate a cyano anthracene such as 9,10 dicyano anthracene, a polystyrene sulphonate and compounds of formulae shown in Figs. 6 and 7. Instead of being a separate layer the electron transmitting material can be mixed with the electroluminescent material to form one layer e.g. in a proportion of 5 to 95% of the electron transmitting material to 95 to 5% of the light emitting

25

30

metal compound.

The electroluminescent layer can comprise a mixture of the light emitting metal compound with the hole transmitting material and electron transmitting material

5

The electroluminescent material can be deposited on the substrate directly by vacuum evaporation or evaporation from a solution in an organic solvent. The solvent which is used will depend on the material but chlorinated hydrocarbons such as dichloromethane and n-methyl pyrrolidone; dimethyl sulphoxide; tetra

10

hydrofuran; dimethylformamide etc. are suitable in many cases. Alternatively electroluminescent material can be deposited by spin coating from solution, or by vacuum deposition from the solid state e.g. by sputtering, or any other conventional method can be used.

15

Preferably the first electrode is a transparent substrate such as a conductive glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a transparent conductive layer such as a metal or conductive polymer can be used.

20

Conductive polymers and conductive polymer coated glass or plastics materials can also be used as the substrate.

25

The second electrode functions as the cathode and can be any low work function metal e.g. aluminium, calcium, lithium, silver/magnesium alloys etc., aluminium is a preferred metal.

30

The display of the invention may be monochromatic or polychromatic. Electroluminescent rare earth chelate compounds are known which will emit a range of colours e.g. red, green, and blue light and white light and examples are disclosed

in Patent Applications WO98/58037 PCT/GB98/01773, PCT/GB99/03619,
PCT/GB99/04030, PCT/GB99/04024, PCT/GB99/04028, PCT/GB00/00268 and can
be used to form OLEDs emitting those colours. Thus, a full colour display can be
formed by arranging three individual backplanes, each emitting a different primary
5 monochrome colour, on different sides of an optical system, from another side of
which a combined colour image can be viewed. Alternatively, rare earth chelate
electroluminescent compounds emitting different colours can be fabricated so that
adjacent diode pixels in groups of three neighbouring pixels produce red, green and
blue light. In a further alternative, field sequential colour filters can be fitted to a
10 white light emitting display.

Either or both electrodes can be formed of silicon and the electroluminescent
material and intervening layers of a hole transporting and electron transporting
materials can be formed as pixels on the silicon substrate. Preferably each pixel
15 comprises at least one layer of a rare earth chelate electroluminescent material and an
(at least semi-) transparent electrode in contact with the organic layer on a side
thereof remote from the substrate.

Preferably, the substrate is of crystalline silicon and the surface of the substrate may
20 be polished or smoothed to produce a flat surface prior to the deposition of electrode,
or electroluminescent compound. Alternatively a non-planarised silicon substrate can
be coated with a layer of conducting polymer to provide a smooth, flat surface prior
to deposition of further materials.

25 In one embodiment, each pixel comprises a metal electrode in contact with the
substrate. Depending on the relative work functions of the metal and transparent
electrodes, either may serve as the anode with the other constituting the cathode.

When the silicon substrate is the cathode an indium tin oxide coated glass can act as
30 the anode and light is emitted through the anode. When the silicon substrate acts as

the anode the cathode can be formed of a transparent electrode which has a suitable work function, for example by a indium zinc oxide coated glass in which the indium zinc oxide has a low work function. The anode can have a transparent coating of a metal formed on it to give a suitable work function. These devices are sometimes
5 referred to as top emitting devices or back emitting devices.

The metal electrode may consist of a plurality of metal layers, for example a higher work function metal such as aluminium deposited on the substrate and a lower work function metal such as calcium deposited on the higher work function metal. In
10 another example, a further layer of conducting polymer lies on top of a stable metal such as aluminium.

Preferably, the electrode also acts as a mirror behind each pixel and is either deposited on, or sunk into, the planarised surface of the substrate. However, there
15 may alternatively be a light absorbing black layer adjacent to the substrate.

In still another embodiment, selective regions of a bottom conducting polymer layer are made non-conducting by exposure to a suitable aqueous solution allowing formation of arrays of conducting pixel pads which serve as the bottom contacts of
20 the pixel electrodes.

As described in WO00/60669 the brightness of light emitted from each pixel is preferably controllable in an analogue manner by adjusting the voltage or current applied by the matrix circuitry or by inputting a digital signal which is converted to
25 an analogue signal in each pixel circuit. The substrate preferably also provides data drivers, data converters and scan drivers for processing information to address the array of pixels so as to create images. When an electroluminescent material is used which emits light of a different colour depending on the applied voltage the colour of each pixel can be controlled by the matrix circuitry.

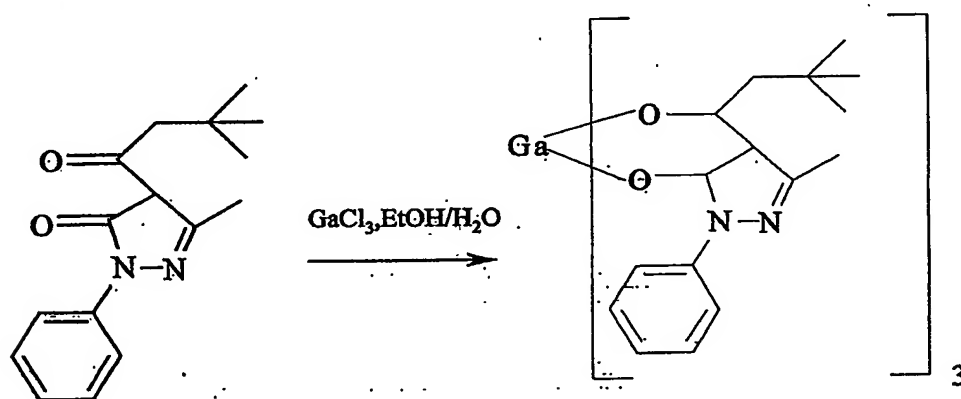
In one embodiment, each pixel is controlled by a switch comprising a voltage controlled element and a variable resistance element, both of which are conveniently formed by metal-oxide-semiconductor field effect transistors (MOSFETs) or by an active matrix transistor.

5

The invention is illustrated in the examples

Example 1

10 **Preparation of Tris-(4-Butylacetyl-3-methyl-1-phenyl-pyrazol-5-onato)Gallium (Ga(BuPz)₃)**



15 4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-one (2.83g, 10.39mmol), in a 100ml round bottom flask, was dissolved in ethanol (~50ml) with gentle heating. Gallium(III) chloride (0.61g, 3.46mmol) was dissolved in H₂O(~10ml) and added to the pyrazolone solution. The resulting suspension was heated to reflux for 2 hours and then allowed to cool. The resulting suspension was filtered and washed with H₂O (3 x10ml) and EtOH (3x10ml) then dried under vacuum at 80°C to give a pink
20 powder with the following analysis.

$\text{Ga}(\text{tBuPz})_3$	C	H	N
Theoretical	65.24	6.50	9.51
Found	65.07	6.57	9.46

Melting point: 252.1°C (D.S.C.)

Emission λ_{max} : 450nm

Photoluminescence Efficiency (x,y): 0.001cdm²μW⁻¹(0.21, 0.24)

5 PL measurement:

PL spectra was measured by Lot Oriel Multispec Model 77400 CCD Camera..

A The measurement was carried out from the powder by spreading the powder on a spectro-sil plate.

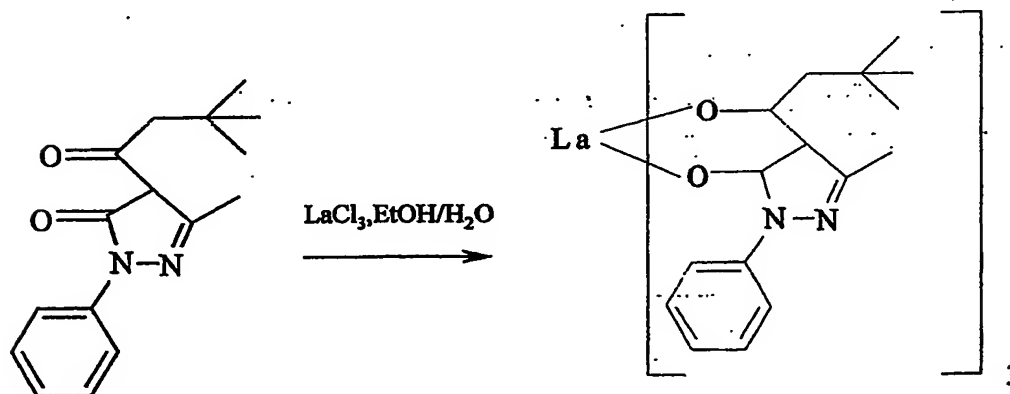
10 Reagents Gallium(III) chloride, anhydrous, 99.99%; Aldrich; 45,089-8

4-tButylacetyl-3-methyl-1-phenyl-pyrazol-5-onato as prepared

Ethanol, denatured with 4.8% Methanol; Fluka; 02857

Example 2

15 Preparation of Tris-(4-tButylacetyl-3-methyl-1-phenyl-pyrazol-5-onato) Lanthanum
(La(tBuPz)₃)



10

Sc(^tBuPz)₃	C	H	N
Theoretical	60.48	6.03	8.82
Found	59.92	6.28	8.67

Emission $\lambda_{\text{max.}}$: 441.8nm

Photoluminescence Efficiency (x,y): 0.003cdm²μW⁻¹ (0.20, 0.22)

15

Lanthanum(III) chloride hexahydrate, 99.9%; Strem Chemicals, 93-5731; Lot no. 251194-S

4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-one as prepared

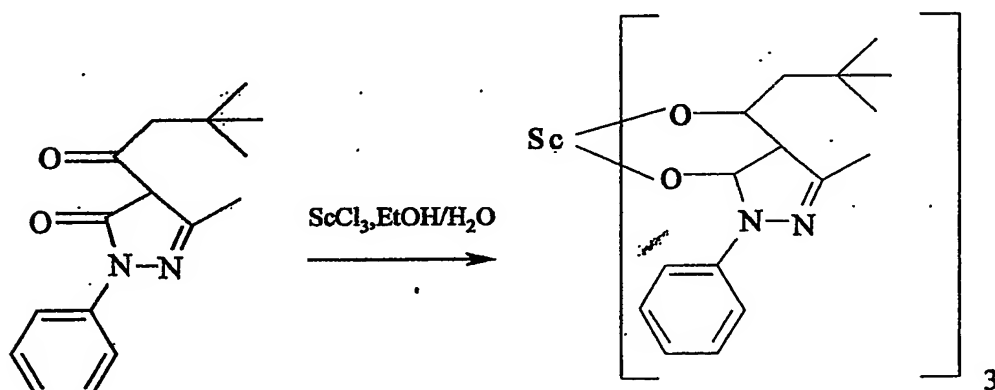
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Ethanol, denatured with 4.8% Methanol; Fluka; 02857.

25

Example 3

Preparation of Tri-(4-^tButylacetyl-3-methyl-phenyl-pyrazol-5-onato)Scandium (Sc(^tBuPz)₃)



5

4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-one (1.07g. 3.93mmol), in a 100ml round bottom flask, was dissolved in ethanol (—50mL) with gentle heating. Scandium(III) chloride hexahydrate (0.34g. 1.31mmol) was dissolved in H₂O (~40mL) and added to the pyrazolone solution. The resulting suspension was heated to reflux for 2 hours and then allowed to cool. The resulting suspension was filtered and washed with H₂O (3 x 10ml,) and EtOH (3 x 10ml) then dried under vacuum at 80°C to give a white powder with the following analysis.

10

Sc(^t BuPz) ₃	C	H	N
Theoretical	67.12	6.69	9.78
Found	66.73	6.65	9.62

15

Melting point: 275.5°C (D.S.C.)

Emission Max.: 448.55nm

Photoluminescence Efficiency (x,y): 0.004cdm²μW⁻¹ (0.22, 0.28)

Reagents

Scandium(III) chloride hexahydrate, 99.9%; Strem Chemicals; 93-2111, Lot no.

20

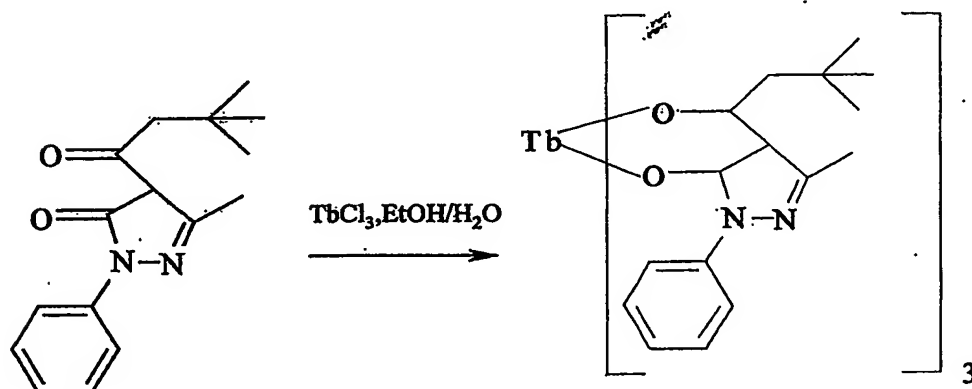
B4745091

4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-one as prepared

Ethanol, denatured with 4.8% Methanol; Fluka; 02857

Example 4

5 Preparation of Tris-(4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-onato)Terbium (Tb(^tBuPz)₃)



10

4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-one (1.45g, 5.32mmol), in a 100ml round bottom flask, was dissolved in ethanol (~50mL) with gentle heating. Terbium(III) chloride hexahydrate (0.66g, 1.77mmol) was dissolved in H₂O (~10mL) and added to the pyrazolone solution. The resulting suspension was heated to reflux for 2 hours and then allowed to cool. The resulting suspension was filtered and washed with H₂O (3 x 10mL) and EtOH (3x10mL) then dried under vacuum at 80°C to give a white powder with the following analysis.

15

Tb(^t BuPz) ₃	C	H	N
Theoretical	59.24	5.91	8.64
Found	59.86	6.23	8.75

20

Melting point: 252.6°C (D.S.C.)

Emission Max.: 492.4nm, 547.6nm

Photoluminescence Efficiency (x,y): cdm²μW⁻¹

5

Reagents

Terbium(III) chloride, 99.9%; Acros

4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-one as prepared

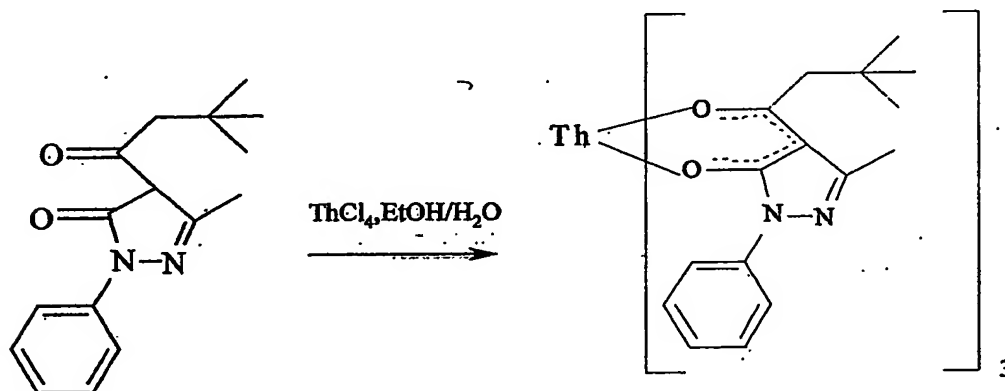
Ethanol, denatured with 4.8% Methanol; Fluka; 02857

10

Example 5

Preparation of Tetrakis-(4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-onato)

Thorium (Th(^tBuPz)₃)



15

4-^tButylacetyl-3-methyl-1-phenyl-pyrazol-5-one (1.92g, 7.06mmol), in a 100ml round bottom flask, was dissolved in ethanol (~50mL) with gentle heating. Thorium(IV) chloride hexahydrate (0.66g, 1.77mmol) was dissolved in H₂O (~10mL) and added to the pyrazolone solution. The resulting suspension was heated to reflux for 2 hours and then allowed to cool. The resulting suspension was filtered and washed with H₂O (3 x 10ml) and EtOH (3 x 10mL) then dried under vacuum at 80°C to give a pink powder with the following analysis.

20

Th(^t BuPz) ₄	C	H	N
Theoretical	58.35	5.81	8.58
Found	58.49	6.06	8.32

Melting point: 254.7°C (D.S.C.)

Emission Max.: 462.8nm

Photoluminescence Efficiency (x,y): 0.002 cdm²μW⁻¹ (0.27, 0.36)

5 Reagents

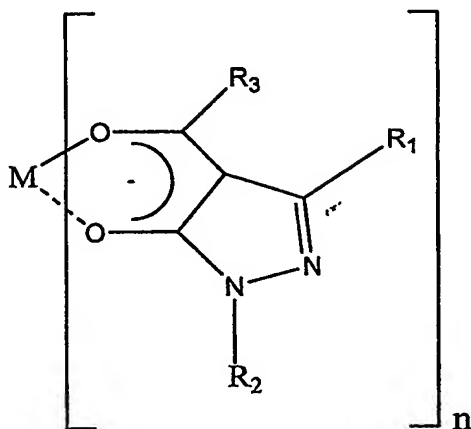
Thorium(IV) chloride hydrate, 99.9%; Strem Chemicals; 09-3155

4-^tButylacetyl-3 -methyl-1 -phenyl-pyrazol-5-one; as prepared

Ethanol, denatured with 4.8% Methanol; Fluka; 02857

Claims

1. An electroluminescent compound which has the formula



(I)

where M is a metal other than aluminium; n is the valency of M; R₁, R₂ and R₃ which may be the same or different are selected from hydrogen, hydrocarbyl groups, substituted and unsubstituted aliphatic groups substituted and unsubstituted aromatic, heterocyclic and polycyclic ring structures, fluorocarbons such as trifluoromethyl groups, halogens such as fluorine or thiophenyl groups or nitrile; R₁, and R₃ can also be form ring structures and R₁, R₂ and R₃ can be copolymerisable with a monomer e.g. styrene.

2. A compound as claimed in claim 1 in which M is gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium, titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium or yttrium.

3. An electroluminescent device comprising (i) a first electrode, (ii) an electroluminescent layer comprising a layer of a complex of formula (I) and (iii) a second electrode.
- 5 4. An electroluminescent device as claimed in claim 3 in which M is gallium, indium, germanium, tin (II), tin (IV), antimony (II), antimony (IV), lead (II), lead (IV) and metals of the first, second and third groups of transition metals in different valence states e.g. manganese, iron, ruthenium, osmium, cobalt, nickel, palladium(II), palladium(IV), platinum(II), platinum(IV), cadmium, chromium.
- 10 titanium, vanadium, zirconium, tantalum, molybdenum, rhodium, iridium, titanium, niobium, scandium, or yttrium and R_3 is a phenyl or substituted phenyl group.
- 15 5. A device as claimed in claim 3 or 4 in which there is a layer of a hole transmitting material between the first electrode and the layer of the electroluminescent complex.
- 20 6. A device as claimed in any one of claims 3 to 5 in which there is a layer of an electron transmitting material between the second electrode and the layer of the electroluminescent complex.
- 25 7. An electroluminescent device which comprises (i) a first electrode, (ii) a layer of a hole transmitting material, (iii) an electroluminescent layer comprising a complex of general formula (I) herein (iv) a layer of an electron transmitting material and (v) a second electrode.
8. An electroluminescent device as claimed in claim 7 in which the hole transmitting layer is an aromatic amine complex.
- 30 9. An electroluminescent device as claimed in claim 8 in which the hole transmitting layer is formed from a poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-

methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD), polyaniline, or a substituted polyaniline.

10. An electroluminescent device as claimed in claim 8 in which the hole
5 transmitting layer has a formula (II) or (III) herein or as in figs. 1 to 4 of the drawings.

11. An electroluminescent device as claimed in claim 8 in which the hole
transmitting layer is a conjugated polymer as herein specified.

10 12. An electroluminescent device as claimed in claim 11 in which the hole
transmitting layer is selected from poly (p-phenylenevinylene)-PPV and copolymers
including PPV, poly(2,5 dialkoxyphenylene vinylene), poly (2-methoxy-5-(2-
methoxypentyloxy-1,4-phenylene vinylene), poly(2-methoxypentyloxy)-1,4-
15 phenylenevinylene), poly(2-methoxy-5-(2-dodecyloxy-1,4-phenylenevinylene) and
other poly(2,5 dialkoxyphenylenevinylenes) with at least one of the alkoxy groups
being a long chain solubilising alkoxy group, poly fluorenes and oligofluorenes,
polyphenylenes and oligophenylenes, polyanthracenes and oligo anthracenes,
polythiophenes and oligothiophenes.

20 13. An electroluminescent device as claimed in any one of claims 7 to 12 in which
the hole transmitting material and the light emitting metal compound are mixed to
form one layer in a proportion of 5 to 95% of the hole transmitting material to 95 to
5% of the light emitting metal compound.

25 14. An electroluminescent device as claimed in any one of claims 7 to 13 in which
the electron transmitting material is a metal quinolate or as in fig. 5 of the drawings.

30 15. An electroluminescent device as claimed in claim 14 in which the metal
quinolate is lithium, sodium, potassium, zinc, magnesium or aluminium quinolate.

16. An electroluminescent device as claimed in any one of claims 7 to 15 in which the electron transmitting material and the light emitting metal compound are mixed to form one layer in a proportion of 5 to 95% of the electron transmitting material to 95 to 5% of the light emitting metal compound

17. An electroluminescent device as claimed in any one of claims 7 to 16 in which the anode and/or cathode is formed on a substrate of crystalline silicon and the surface of the substrate may be polished or smoothed to produce a flat surface prior to the deposition of electrode, or electroluminescent compound.

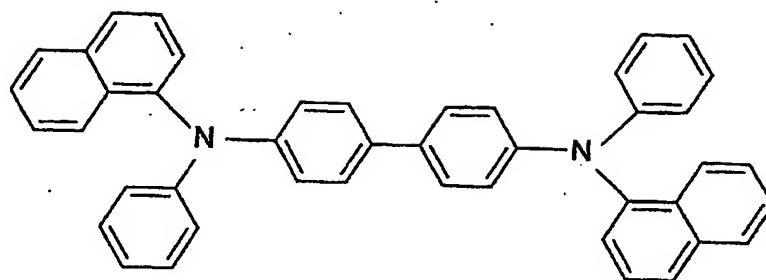
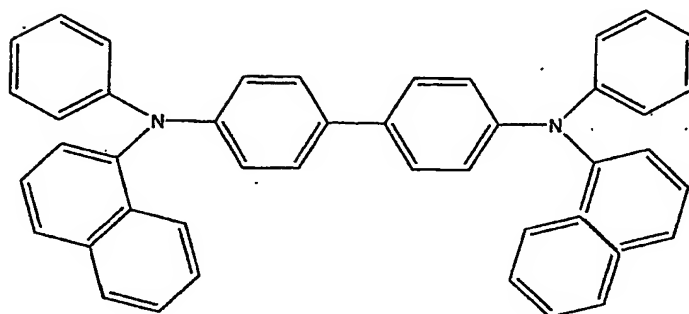
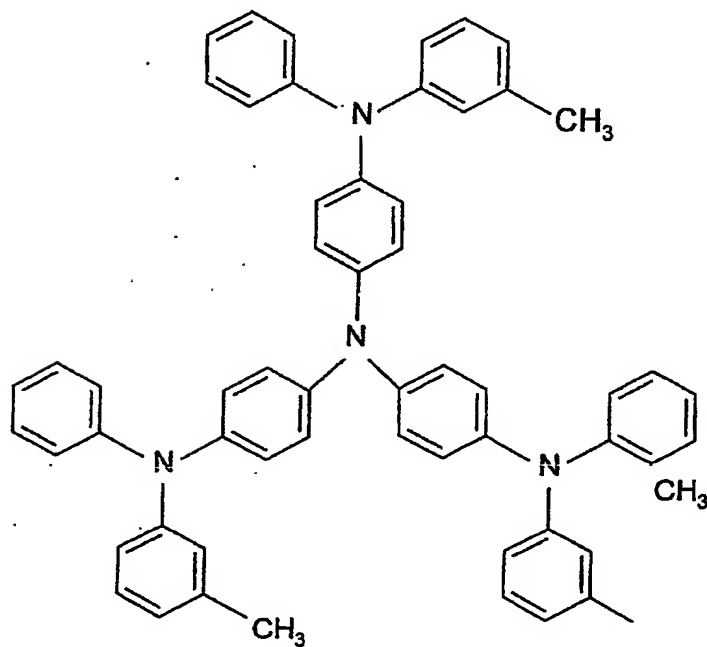
18. An electroluminescent device as claimed in any one of claims 7 to 16 in which the anode and/or cathode is formed on a substrate of a non-planarised silicon substrate.

19. An electroluminescent device as claimed in any one of claims 3 to 18 in which there is a copper phthalocyanine layer on the first electrode and a lithium fluoride layer on the second electrode.

- 24 -

Abstract

An electroluminescent material is a metal complex of 1-phenyl-3-methyl-4-trimethylacetyl pyrazol-5-one.

 α -NPB β -NPD

mTADATA

Fig. 1

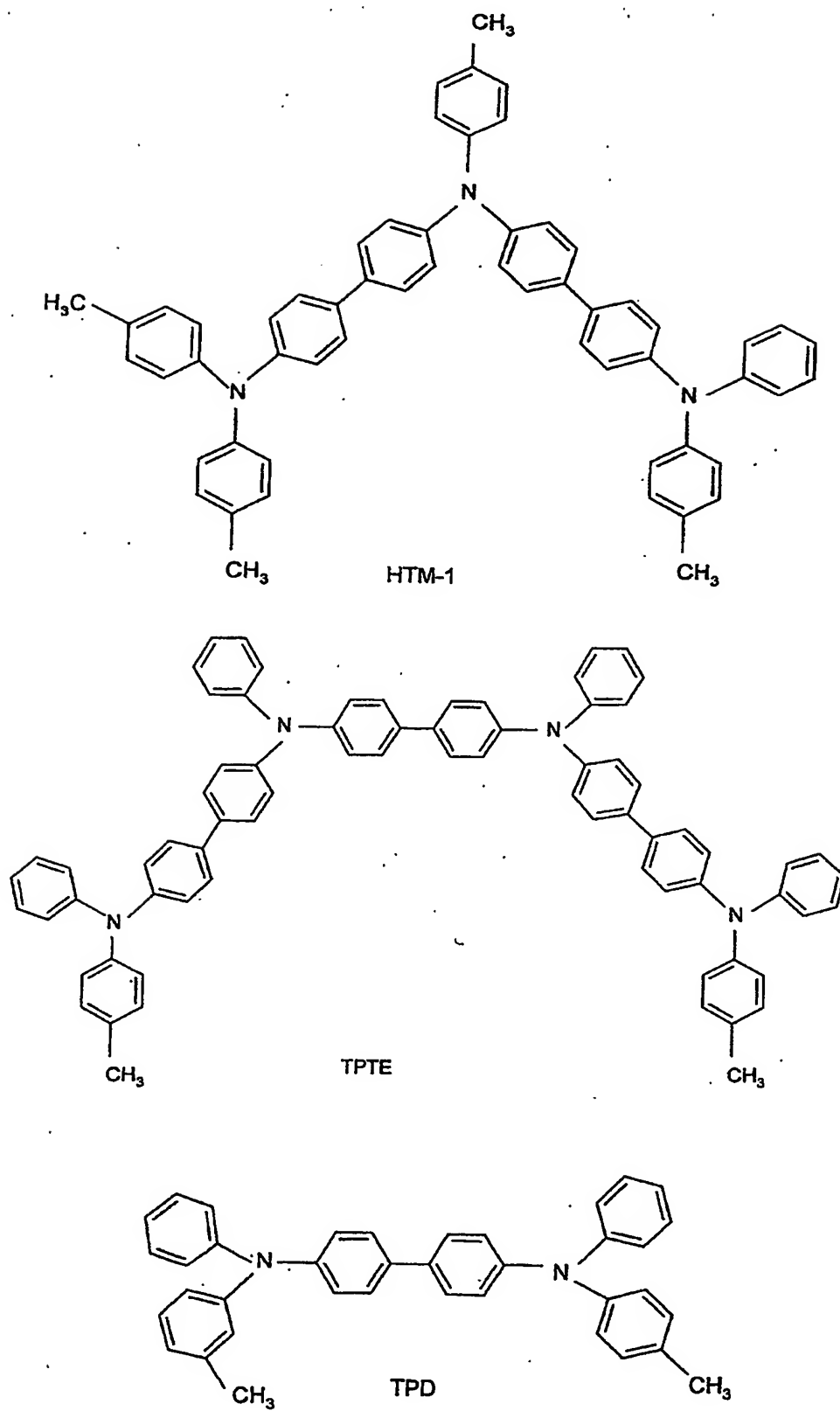


Fig. 2

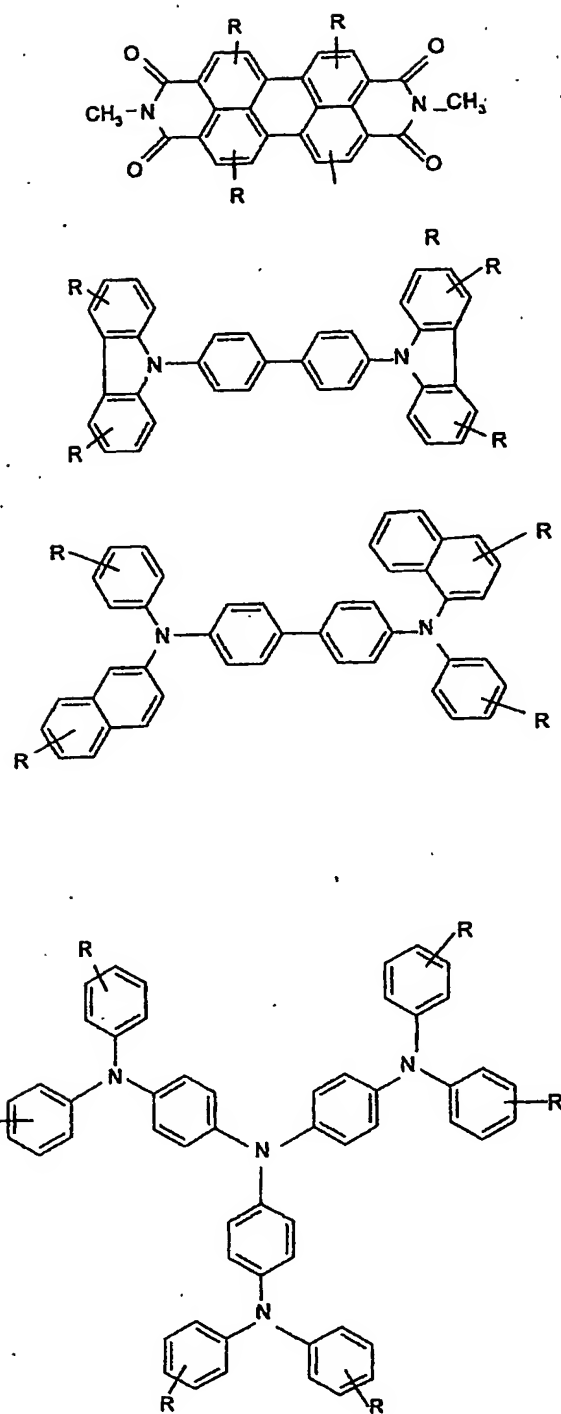


Fig. 3

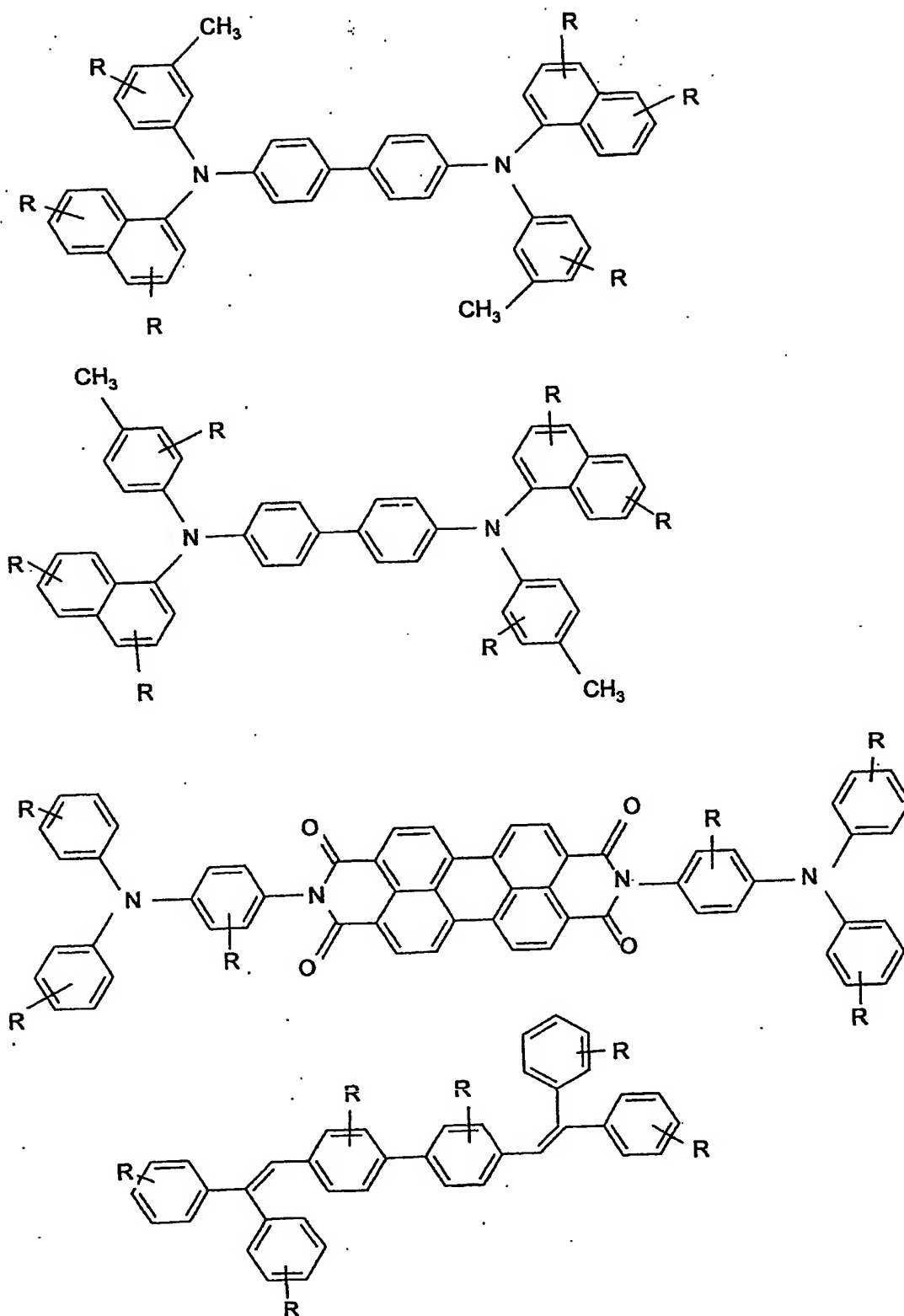
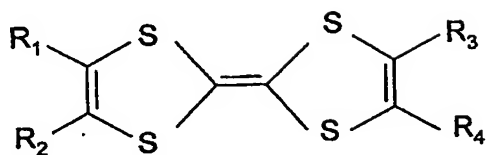
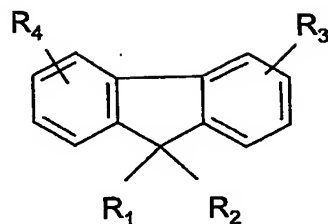
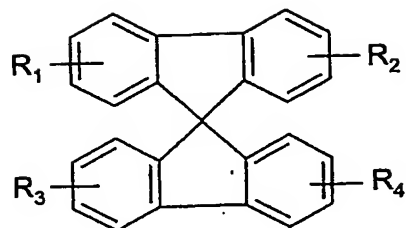


Fig. 4



or

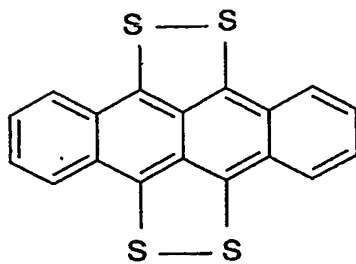
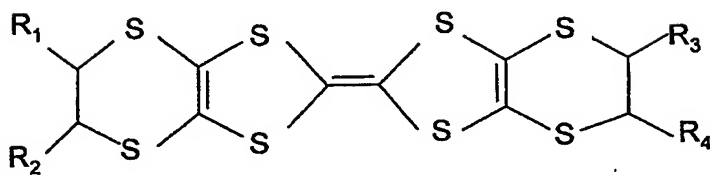
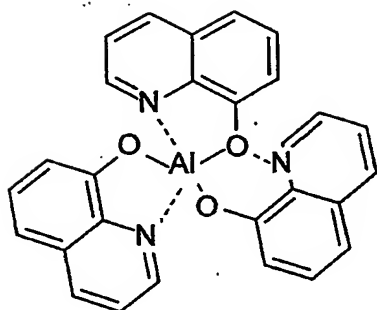
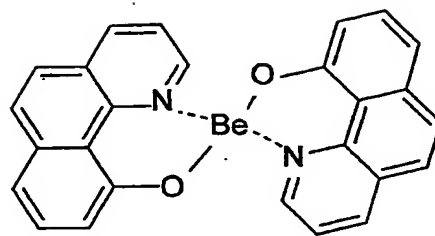


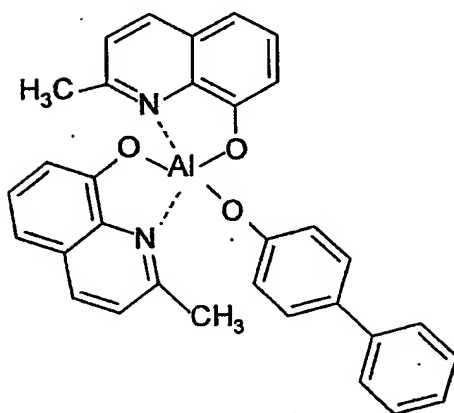
Fig. 5



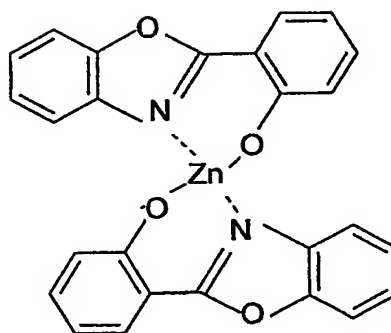
Alq



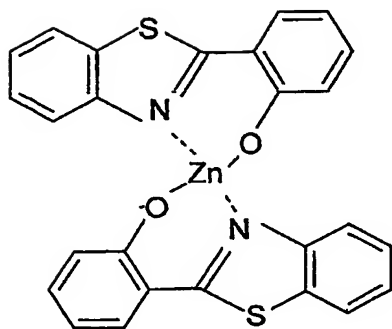
Beq



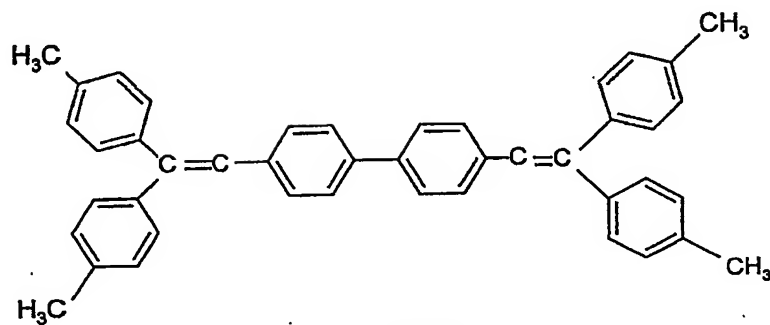
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ZnPBO

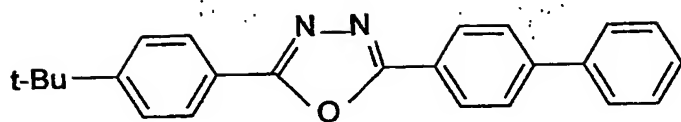


ZnPBT

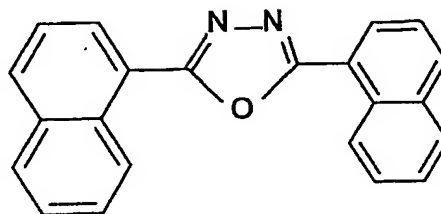


DTVb1

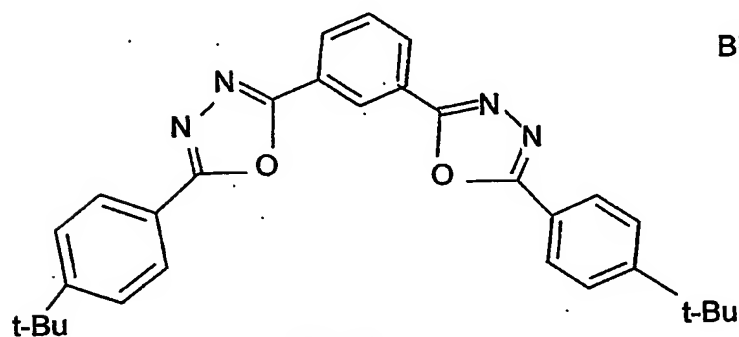
Fig. 6



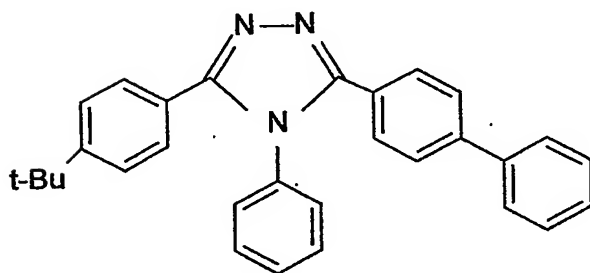
t-Bu-PBD



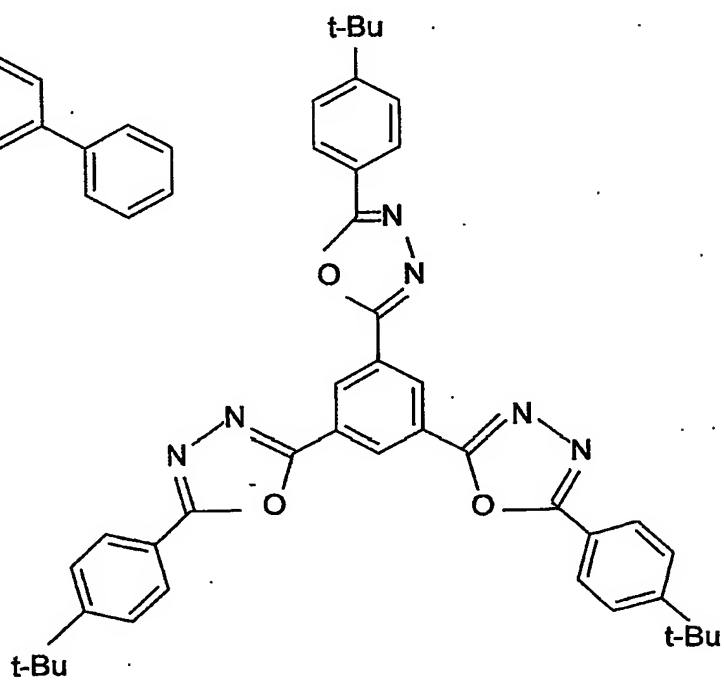
BND



OXD-7



TAZ



OXD-Star

Fig. 7

PCT Application
GB0305303

